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Spin-orbit splitting of the valence bands in silicon determined by means of high-resolution photoconductive spectroscopy

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We present the first high-resolution photoconductive observation of the transitions associated with the resonant impurity states of residual boron in very-high-purity float-zone silicon single crystals at different low temperatures. According to the energies of the transitions from the ground state to the impurity states related to the $p_{1/2}$ valence band, and taking the nonparabolicity of the split-off valence band into consideration, we determine the ionization energy of the boron acceptor to the spin-orbit split-off valence band very accurately as 88.45 ± 0.01 meV. The spin-orbit splitting of the valence bands in silicon is also deduced to be 42.62 ± 0.01 meV.

The accurate experimental determination of band parameters and related quantities is always very important for the basic understanding of the band structure and practical application of materials. Even for silicon, which is a widely used semiconductor material and probably one of the most important chemical elements for electronic industry and human life today, there are still not enough accurate values of some parameters for some purposes. We take the spin-orbit splitting of the valence bands as an example. The spin-orbit splitting for Si (Ref. 1) is small (around 40 meV), and has usually been determined from the transition energies of group-III acceptors from the ground state to the resonant impurity states associated with the spin-orbit split-off valence band by use of infrared (ir) absorption spectroscopy.[2-5] These measurements gave values of $\Delta_0(\mathrm{Si}) = 42.62 \pm 0.04$ meV (Ref. 4) or 44.00 ± 0.02 meV (Ref. 5) (i.e., 1.4-meV difference between two recent determinations). It is not easy to improve the accuracy of the determination because of the lower sensitivity of the method as compared with what will be discussed below. Furthermore, one needs relatively higher impurity concentration (at least 10^{16} cm^{-3}) for observing the transitions to the localized impurity states in the energy gap and to the resonant states in the valence band. Thus, the measured results may be modified by impurity effects at higher concentrations.

Photothermal ionization and photoconductive spectroscopy[6] have much higher sensitivity than the ir absorption technique and become powerful tools to investigate and identify residual shallow impurities and their complexes in ultra-high-purity semiconductors.[7,8] These methods also have very high resolution. The photoconductive response of a shallow acceptor (e.g., boron) in silicon is generally based on optical excitation followed by ionization of the bound holes at the excited states related to the $p_{3/2}$ and $p_{1/2}$ band by phonon absorption to the corresponding valence band (photothermal ionization) and relaxation of the excited holes at the resonant states or the $p_{1/2}$ band by phonon emission to the $p_{3/2}$ valence band (refer to Fig. 1 where E_I and E_I^* are the ionization energies of the acceptor from its ground state to the $p_{3/2}$ and $p_{1/2}$ valence bands, respectively, and Δ_0 is the spin-orbit splitting of the valence bands). We present in this paper the first high-resolution photoconductive investigation of the transitions from the ground state to the $p_{1/2}$-valence-band–related excited states of residual boron in very-high-purity float-zone silicon single crystals. From this investigation the $p_{1/2}$-series ionization energy is obtained more accurately. Furthermore, the spin-orbit splitting of the valence bands in silicon is deduced to be 42.62 ± 0.01 meV with high accuracy.

The high-purity silicon samples investigated, with a size of $10 \times 10 \times 10$ mm^3 and residual boron concentration of 10^{11}–10^{13} cm^{-3}, were cut from single-crystal ingots grown by a vacuum float-zone technique. After being lapped with SiC powders and etched in a HF-HNO_3 solution, the samples were implanted with a low-energy B^+ ion beam on the surface layers for contacts, followed by

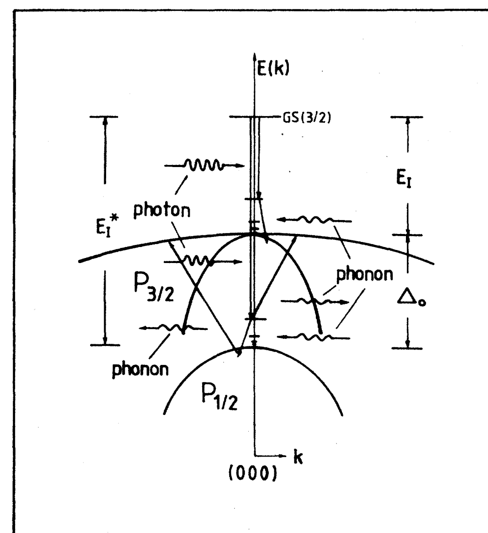

FIG. 1. Schematic diagram showing photoconductive processes of an acceptor in silicon.

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lamp annealing to remove the implantation damage and to activate the dopants rapidly. The possible oxide layers on the sample surfaces were removed by a dilute HF etchant before fresh indium foils were pressed firmly onto the opposing implanted faces. At last, the contacts were formed by soldering thin enamel-isolated copper wires onto the In foils. The *I-V* measurements showed that the contacts were Ohmic down to temperatures as low as 4.2 K.

Based on a vacuum-type Nicolet-200SXV Fourier-transform spectrometer, our measurement system has the following components: a light source and a Michelson interferometer, a temperature-variable Oxford optical cryostat in which the sample can be mounted in a stress-free way on a sample holder with a 107-Ω carbon resistor for temperature sensor and a heater for changing sample temperature inside, a tunable bias electronics, an ultra-low-noise preamplifier with band-pass filters, and an IR-80 computer for data acquisition, processing, and storage. The temperature can be changed from 300 to 4.2 K and can be stabilized to ∓0.2 K by careful control of the liquid-helium flow rate and the heating current.

High-resolution photoconductive measurements were performed on three high-purity float-zone silicon samples, Nos. 1, 2, and 3 with room-temperature resistivities of 1000, 4000, and 40 000 Ω cm, respectively, at a resolution of 0.25 cm^{-1}. All the measured samples show similar features to those plotted in Fig. 2, which shows relative photoconductive spectra of sample No. 1 at 9.3, 18.0, and 27.1 K. The figure is plotted in such a way that the broad continuous bands of all three curves share exactly the same shape in order to illustrate the temperature dependence of the lines. We can see three distinct peaks labeled $2p'$, $3p'$, and $4p'$ whose positions generally coincide with those of the $p_{1/2}$ lines reported in the ir absorption spectra of boron[2-5] at much higher concentration than the samples used in this paper. From the temperature dependence of the peaks, the thermal relaxation processes of the excited holes at the resonant states or from the $p_{1/2}$ band to the $p_{3/2}$ band by phonon emission are apparently dominant in this case. Listed in Table I are the line positions of the $p_{1/2}$ series for sample No. 1 at different temperatures. Taking the nonparabolicity of the $p_{1/2}$ valence band into consideration, we may express the np' line energy $h\nu$ as (Ref. 2)

$$h\nu = E_I^* - \left[\frac{m_{SO}^*}{m_0}\right]\left[\frac{R_H}{\epsilon^2}\right]\left[\frac{1}{n^2} - \lambda\left[\frac{8}{3n^3} - \frac{3}{n^4}\right]\right], \quad (1)$$

where

$$\lambda = \left[\frac{2(B^2 + C^2/5)}{A^2}\right]\left[\frac{m_{SO}^*}{m_0}\right]\left[\frac{R_H}{\epsilon^2\Delta_0}\right] = 0.396\,,$$

and $R_H = 13.6$ eV is the ionization energy of hydrogen atom. m_{SO}^*/m_0 and ϵ are the hole effective mass of the split-off band and the dielectric constant, while A, B, and C are the valence-band parameters and Δ_0 is the spin-orbit splitting of the valence bands of silicon, respectively. The most precise experimental values of the above parameters published so far[9] have been chosen in the evaluation of the magnitude of λ. From the intercept on the energy coordinate of the plot of the best linear fitting to Eq. (1), the $p_{1/2}$-series ionization energy, E_I^*, of boron is deduced directly to be 713.37 ± 0.08 cm^{-1} (88.45 ± 0.01 meV) with probably the highest accuracy up to now. If we use either the uncorrected Rydberg series ($\lambda = 0$), or the value $\lambda = 0.339$ first used by Zwerdling *et al.*,[2] as many authors did, we get the value of E_I^* to be 88.36 and 88.43 meV, whose differences from our present result, 88.45 meV, are beyond our worst experimental error.

The spin-orbit splitting can be easily obtained if we also know the $p_{3/2}$-series ionization energy E_I whose accurate experimental determination should be and can be improved. Conventionally, E_I is deduced by adding the theoretical binding energy of line 4 (6.1 meV) (Ref. 10) or line 6 (3.67 meV) (Ref. 11) to the corresponding line energy. However, Fischer and Rome[5] reported a direct experimental value of 44.39 ± 0.02 meV according to the position of the background break in the ir absorption spectra of boron. However, we have observed distinct and discrete lines at higher energies than this value in the high-resolution photothermal ionization (PTI) spectra of the same samples used in this study at 8.0 K,[12] which means that the actual value of E_I(boron) should probably be greater than 44.39 meV. Consequently, addition of the binding energy of the higher excited state, whose "central-cell effect" can be negligible, to the corresponding transition-line energy seems still to be a more reason-

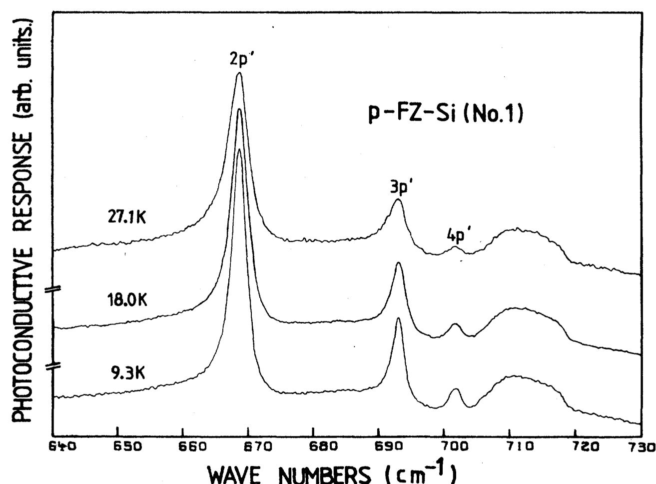

FIG. 2. High-resolution photoconductive spectra of sample No. 1 (room-temperature resistivity is 1000 Ω cm) at 9.3, 18.0, 27.1 K. (The continuous bands of the curves have exactly the same shape for demonstrating the temperature dependence of the peaks). Instrumental resolution is 0.25 cm^{-1}.

TABLE I. Line positions of $2p'$, $3p'$, and $4p'$ in the photoconductive spectra of sample No. 1 at different low temperatures. The biggest error is 0.08 cm^{-1}. Unit is cm^{-1}.

T (K)	9.3	10.0	13.4	18.0	21.2
$2p'$	668.64	668.59	668.59	668.62	668.67
$3p'$	692.94	692.98	693.02	692.99	692.92
$4p'$	701.79	701.62	701.81	701.71	701.64

able way to determine the value of E_I. Thus, from our high-resolution PTI data of sample No. 1, whose line 6 is at 42.16 ± 0.01 meV, the $p_{3/2}$ series ionization energy of boron is yielded as $E_I(\text{boron}) = 45.83 \pm 0.01$ meV. Then the spin-orbit splitting of the valence bands in silicon is obtained to be $\Delta_0(\text{Si}) = E_I^* - E_I = 42.62 \pm 0.01$ meV, which seems to be the most accurate value so far. An even more precise experimental determination needs more careful calculation of the binding energy of higher excited states or better direct determination of the binding energy of the ground state of acceptors.

In conclusion, high-resolution photoconductive spectroscopy has been successfully applied to observe the $p_{1/2}$ series transition of residual boron acceptors at concentrations of 10^{11}–10^{13} cm^{-3} in very-high-purity float-zone silicon samples at different low temperatures for the first time, to the best of our knowledge. The $p_{1/2}$ ionization energy of boron is determined more accurately to be 88.45 ± 0.01 meV. From the experimental data, the spin-orbit splitting of the valence bands in silicon is deduced to be 42.62 ± 0.01 meV.

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